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VANADIUM DIOXIDE PROTECTIVE DEVICES

- FINAL TECHNICAL REPORT

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ABSTRACT

The subject of this contract was the development of vanadium dioxide optical switches. The aim was to further develop the reactive sputtering process for deposition of vanadium dioxide, originated by Dr.K.L.Lewis et al at The Royal Signals and Radar Establishment, England and developed by OCLI Optical Coatings Ltd, and manufacture devices for evaluation by the United States Army.

The process has been extensively investigated and optimised throughout the contract to the extent that good switching vanadium dioxide can now be reliably produced. Vanadium dioxide can now be deposited on germanium as well as silicon and has been fully characterised. The process stability, repeatabilty and the quality of the vanadium dioxide has been significantly improved. In particular the optical scatter has been reduced and the dynamic range has been increased

Devices incorporating vanadium dioxide have been manufactured to the required specification and indications are that the devices should fulfill their intended purpose. OCLI will continue to develop these devices and field trials are recommended. Keywords:

KEYWORDS

Vanadium dioxide, optical switch, laser hardening. (AW)

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1. INTRODUCTION

This development contract has been carried out in order to answer the increasing requirement for protection of sensitive infrared detectors from pulsed laser radiation in the military environment. Although other applications are possible it has been the concern of this project to develop a protective device for use in the 8-12 micron wavelength region.

The approach in this case has been to exploit the well established optical properties of vanadium dioxide thin films in the infrared. Such films have been shown to undergo a transition from monoclinic to tetragonal symmetry at a temperature of about 68 degrees Celsius (Refs.1-5). Accompanying this there is a change of phase from semiconductor to metal. In the infrared waveband this manifests itself as a large decrease in transmission and an increase in reflection. Published work has indicated that a variety of methods exist for the deposition of stoichiometric vanadium dioxide films, among which the most successful appears to be reactive sputtering (Ref. 5). OCLI had developed a radio frequency (R.F.) planar magnetron sputtering system, incorporating a number of novel process control mechanisms, using private venture funding prior to the award of this contract. This formed the basis for the development work of this contract and has resulted in the production of vanadium dioxide comparable in optical terms with the best published values and significantly superior to those prepared by OCLI prior to the contract. This report presents in detail the equipment and methods used to obtain thin films of vanadium dioxide for incorporation in protective devices.

A significant development effort has been directed at the inclusion of switching films in antireflection coatings for the 8-12 micron band. As part of this work a number of fully coated devices have been designed and produced for evaluation. The basic structure of these trial devices is that of a germanium window with both faces antireflection coated. One of the faces in the case of each device has a vanadium dioxide film which provides the protective action. Testing of materials and devices has been undertaken for both diagnostic and functional purposes. Full test data has been accumulated for trial devices and is presented in a separate report for comparison with the target specification.

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2. VANADIUM DIOXIDE FILM DEPOSITION

2.1 System Description

The vanadium dioxide has been produced using a Leybold-Heraeus Z550M R.F. magnetron sputtering system which has been suitably modified for the process. The system chamber is approximately 550 mm in diameter and incorporates three ports in it's top in which can be fitted 200 mm diameter R.F. magnetrons or radiant heaters in any combination. The substrate table is a large turntable in the base of the unit. i.e. it has a sputter down configuration.

The pumping system consists of a 450 l/s turbomolecular pump backed by a rotary pump. A liquid nitrogen cold trap is also included along with a manually operated downstream throttle valve. Normally the gases are delivered via MKS type mass flow controllers to a common manifold where they are mixed before passing to the chamber. For the deposition of vanadium dioxide the gas delivery system was modified so that the gases were delivered to the unit separately. The process pressure is measured using a MKS Baratron capacitance monitor, type 220B.

The R.F. generator has a rated power of 2.5kW. Matching networks ensure that the reflected power is less than about 10W.

Initially a simple substrate table about 100 mm square was used which was heated from below using an array of quartz lamps. The table temperature was measured using a thermocouple and the complete table sat directly on top of the turntable in the base of the chamber. This meant that the turntable could not be rotated, with the consequent decrease in thickness uniformity, and a limit of only about 5 substrates able to be coated at one time. This was subsequently changed (see section 2.3.2).

2.2 OCLI System and Process Development Prior to Award of Contract

OCLI developed a number of techniques to improve the process stabilty and control prior to the award of this contract. These are briefly described in the original proposal and are confidential to OCLI.

2.3 System and Process Development Throughout this Contract

This section details the developments of the system and process throughout the period of this contract.

2.3.1 Deposition Conditions

Initial deposition conditions were selected by reference to published literature and previous work at OCLI. It was already known that the formation regime for stoichiometric vanadium dioxide films was very sharply defined and would require exceptional means to establish control. In particular the flow of argon and oxygen gases throughout the process had to be regulated to a very fine degree. The substrate heating and power to the R.F. planar magnetron were also critical variables in the process.

It was established that the successful deposition conditions for vanadium dioxide would probably lie in the following region;

Substrate temperature:	400-450 degrees Celsius
Oxygen input:	1%-10% of argon input
R.F. power:	1.5-2.0 kW

Some indication of the effect of each parameter within the range was also obtained from literature.

As a first step films were produced for evaluation at an indicated temperature of 450 degrees C, heated indirectly by the quartz lamps mounted beneath the small square substrate table. Sample films were deposited on glass, silicon and germanium substrates. At this point in the project the emphasis was on producing the maximum optical transition in the infrared. A number of good switching samples were produced on germanium substrates, thus providing a basis for refinement. Having established a basic regime for deposition of vanadium dioxide, the project then turned to refinement of the process and improving the process repeatability.

2.3.2 Substrate Heating

A major cause of plasma instability was found to be connected with the quartz lamps used to heat the substrates, and their associated power leads. Without the heaters operating the plasma stability was significantly improved. In an effort to overcome this problem an array of infrared heaters was installed in the top of the chamber, remote from the plasma. This required the use of the original rotating substrate table supplied with the coating machine. Unfortunately, the plasma instability was still present.

The system's original resistive element radiant heater was refitted. This had no heater supply leads within the chamber and was effectively screened. Using this heater the plasma stability was significantly improved, but the heater was incapable of heating the substrates to a sufficiently high temperature (>400 degrees Celsius). Two radiant ring heaters were manufactured which were capable of providing more than 4 kW of heating to the table which proved more than adequate. With this heater configuration the plasma stability was greatly improved. In addition the capacity of the machine was greatly increased and uniformity improved. The system can now accommodate ~50 25mm diameter substrates compared with four using the original small square substrate table.

Because this heater configuration required the substrate table to be rotated, the substrate table temperature could no longer be measured directly. The thermocouple was moved to a position just above the substrate table midway between the two heaters. This necessitated re-optimisation of the process temperature. Sample films deposited using the previously identified process temperature indicated, by their poor optical transition, that the actual substrate temperature was significantly lowered.

2.3.3 Modifications to Rotating Substrate Table

Because of the high power of the new heaters, the water cooled rotating substrate table overheated resulting in water leaks and ultimately a weld failure. A new solid stainless steel table was manufactured in an effort to overcome this problem. This degraded the process stability. It was concluded that the instability was caused by inconsistent and uneven coating of the table with vanadium. This would cause the oxygen gettering rate to vary as the table rotated resulting in a varying oxygen partial pressure.

The original plated copper table was re-fitted but without any water cooling which resolved the instability problem.

2.3.4 Optimum Process Conditions and Deposition Cycle

The effects of varying the various deposition parameters on the coating characteristics was investigated in order to optimise the coating performance. Plasma pressure, R.F. power, argon flow, oxygen flow and process temperature were all investigated.

Typical conditions for optimum vanadium dioxide are summarised in Table 1. It should be noted that these

conditions apply to the system used and the current configuration of the system. Producing the material in another system or after modifications to the system could require significantly different conditions. Changes to the pumping speed, substrate-target spacing, system surface area (i.e. gettering surface area) and gas distribution can all affect the deposition conditions.

3. CHARACTERISATION OF VANADIUM DIOXIDE FILMS

3.1 Optical Constants of Vanadium Dioxide

The transmission characteristics of sample films were measured in both hot and cold conditions using a Perkin-Elmer model 983G spectrophotometer. This was the most immediate diagnostic aid in coating development. Deposition parameters were adjusted on a day to day basis using this data.

The aspect of greatest interest is the transition from high to low transmission in the 8-12 micron region. In stoichiometric vanadium dioxide this is reported to take place at a temperature of 68 degrees Celsius. The change in the extinction coefficient (k) is nominally from 0.2 to 7.0 in the waveband of interest and the real component of the refractive index (n) is reported to lie in the range 2.8 to 3.0 at all temperatures (Ref. 6). For films of about 0.5 microns thickness this would represent a transition to less than 1% transmission.

All films produced were transmisson tested at low and high temperatures. While the deposition process has developed to the point that almost every run produces switching material, it is not found that all samples switch down to less than 1% transmission. This is mainly due to the presence of mixed oxides. When this occurs it is often accompanied by a loss of some room temperature transmission also. An illustration of this behaviour is given in Figs. 1 and 2. At present ~40% of vanadium dioxide produced has optimum switching characteristics.

The presence of absorption bands in the 10 to 16 micron region is another indication of mixed oxide composition. In the fine tuning of the process it was found that these bands in particular could be removed by raising the substrate temperature.

While sample films were produced which displayed switching action at the published temperature of 68 degrees C, the better films were found to switch at a lower temperature

(~55 degrees C). This indicates a slight excess of vanadium present in the film.

In order to estimate the n and k values of vanadium dioxide films it was also necessary to augment hot and cold transmission data with hot and cold reflection data. An example of the values observed is given in Fig. 3. Typical data obtained indicate a k value of 6.5 to 7.0 for efficient switching films at 10.6 microns when heated. The n and k values at room temperature were more difficult to estimate reliably but appear to be about 3.0 and 0.3 respectively, by derivation from measurements of film thickness made using a stylus instrument and from spectrophotometric data. Both n and k are highly dispersive in the 8 to 12 micron region and vary noticeably with temperature in the unswitched condition.

3.2 X-ray Diffraction

A very useful way of determining film structure is to study the X-ray reflection diffraction angles. The characteristic reflection angles and their associated lattice spacings are known for many crystalline oxides of vanadium. It should be noted however that the relative intensities observed vary from those published due to the high degree of orientation found in films produced by this deposition method.

It was found that in a group of samples which displayed switching action to a varying degree each film exhibited a characteristic vanadium dioxide reflection peak. Better films were found to be almost pure stoichiometric vanadium dioxide in structure, having only one reflection peak in the angle range tested. Other films of poorer optical performance exhibited reflection peaks at additional angles associated with mixed oxide lattices. This data confirmed that the most efficient switching films did indeed possess a highly ordered vanadium dioxide lattice structure even though the optical transition occurred at a lower temperature.

3.3 Surface Profilometry

The texture of coated surfaces was assessed using a Sloan Dektak model 3030. This is a stylus instrument with a 12.5 micron tip capable of 0.1 nm vertical resolution. Surface roughness was given attention due to the belief that the resistance to laser damage was limited mainly by this feature of the films. The typical peak to valley roughness of good switching films was found to be about 10 nm. This was very much greater than the roughness of the substrate or any other conventional infrared optical coatings which were

deposited for the project. The visible wavelength scatter of the vanadium dioxide films is noticeably greater than that normally experienced in optical coatings but does not appear to significantly reduce infrared transmission or switching performance. It is however likely that the scatter at visible wavelengths is symptomatic of a surface structure which could limit the laser damage threshold. For this reason it would be valid for future development effort to be given to this topic.

4. PROTECTIVE DEVICE DEVELOPMENT

4.1 Design of Coatings

The basic concept of device development has been to construct all candidate devices by overcoating conventional dielectric films on to vanadium dioxide layers which have been sputtered onto germanium substrates. The design substrate was a plane parallel germanium window with a high efficiency antireflection coating on one face and the device coating on the other. A number of possible device coating structures were considered.

4.1.1 Single Layer Overcoating

A simple way of increasing the transmission of the device was to overcoat the vanadiun dioxide film with a single layer of zinc sulphide. This combination provides a low efficiency antireflection coating but has the advantage of simplicity and can provide diagnostic information about the n and k values of the vanadium dioxide film. The ultimate device transmission and reflection specifications would not be met by the coating. The theoretical characteristics of such a device are shown in Fig. 4.

4.1.2 Single Layer Equivalent Overcoating

While the single layer coating failed to meet the requirements of the target specification it was believed possible to construct a suitable device using a multilayer overcoating with equivalent properties to those of an ideal quarter-wave matching layer. A multilayer stack of zinc selenide and thorium fluoride was designed to simulate a layer of intermediate refractive index and having quarter-wave optical thickness in the 8-12 micron region. One of the aims of this design study was to investigate the degree of reflection which could be obtained from a device in the activated state. The coating was optimised and Figs 5 to 7 show transmission, reflection and vector amplitude characteristics. This provided a datum for comparison with

other possible designs.

4.1.3 Two Layer Overcoating

A two layer overcoating was designed to maximise cold state transmission. The coating provides low reflection in accordance with the target specification. The layer materials used are zinc selenide and thorium fluoride in this case. In the cold state the antireflection performance of the overall device is such that the transmission is restricted only by the absorption loss in the vanadium layer. In the activated condition the device coating has a higher theoretical reflection of 10.6 micron radiation than the single layer equivalent coating. The derived characteristics of this device are shown in Figs. 8 and 9.

4.1.4 Three Layer Overcoating

A further design alternative was introduced which reduces sensitivity to variations in the thickness and k value of the vanadium dioxide film. The overcoating also contains features which act to improve cosmetic and environmental properties. Germanium, zinc sulphide and thorium fluoride are the layer materials used in the structure. In the cold state the device has good reflection and transmission characteristics while in the activated state it has comparable reflection to the two layer overcoating. The theoretical properties of the coating are presented in Figs. 10 and 11.

4.2 Preparation of Trial Devices

4.2.1 Rear Face Antireflection Coating

The antireflection coating applied to the passive face of all sample devices is the OCLI high efficiency coating for germanium No. 6040008. This is an established antireflection coating for internal surfaces of germanium optical components for use in the 8 to 12 micron band. The residual reflection from this surface of sample devices lies in the range 0.2% to 0.3%.

4.2.2 Two Layer Overcoated Device

The two layer overcoating was deposited using conventional evaporation methods. A group of sample vanadium dioxide films with approximately 0.4 microns thickness were included in the runs. The resultant transmission was slightly lower than expected from these trials and turned out to be due to a variation in the optical constants and thickness of the vanadium dioxide layers. The transmission and reflection

measurements from a typical sample are shown in Figs. 12 and 13. The mismatch in the coating is evident in the reflection curve and accounts for the reduction in transmission.

4.2.3 Three Layer Overcoated Device

This sample group was coated in the same vacuum system as the two layer device overcoatings. The only significant process difference being the addition of a germanium layer which was deposited by electron evaporation. Further to the optical interference properties of the germanium layer it was expected that this would act as a low loss adhesion layer for the overcoating. The general performance of the coating was more acceptable than the two layer overcoating. Both reflection and transmission characteristics exceeded the target specification. Spectrophotometric data are given in Figs. 14 and 15.

4.3 Characterisation of Devices

4.3.1 Optical Transition

The trial devices constructed for evaluation in the course of this project all incorporated vanadium dioxide films with good switching behaviour. It was of interest to determine if there were any change in the properties of the active film material as a result of further vacuum processes.

The overcoating of the vanadium dioxide with thermally evaporated matching layers, and the deposition of an antireflection coating on the rear face of the substrate, did not measurably effect the rejection ratio of the vanadium dioxide (room temperature transmission/ hot transmission) or the transition temperature. Obviously the reduction of reflection losses increased the room temperature transmission significantly.

Another area of interest was the transition temperature. This proved to be unchanged by the overcoating processes. An example of a device transition curve is given in Fig. 16.

4.3.2 Pulsed Laser Characterisation

These results are presented in a separate report on device performance.

8. ACKNOWLEDGEMENTS

The authors acknowledge the invaluable assistance of Mike Meehan in developing the coating system and Chris Hale for his original work on this topic.

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6. H.A.MacLeod, W.E.Case and M.K.Purvis, Topical Meeting on Optical Interference Coatings, Monterey (1984).

TABLE 1

Typical Deposition Conditions for Vanadium Dioxide

Subs.-Target (mm)	Ar Flow Rate (sccm)	O_2 Flow Rate (sccm)	O_2 Partial Press. (μm)	Total Press. (μm)	R.F. Power (W)	Subs. Temp.* (°C)
125	100	~5	~1	30	2000	~500

* The substrate temperature cannot be measured directly. The value quoted is the temperature indicated by a thermocouple positioned just above the substrate table.

FIGURE 1

Hot and Cold Transmission of Sample Film
of Stoichiometric Vanadium Dioxide

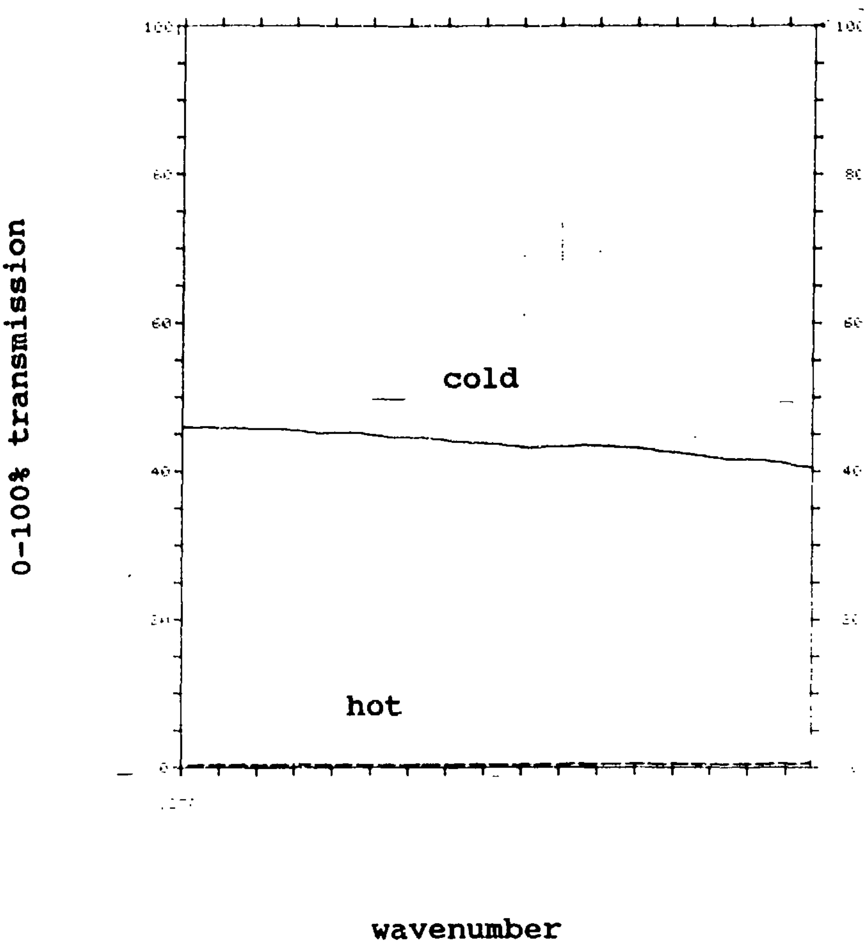

FIGURE 2

Hot and Cold Transmission of Sample Film of Mixed Vanadium Oxides

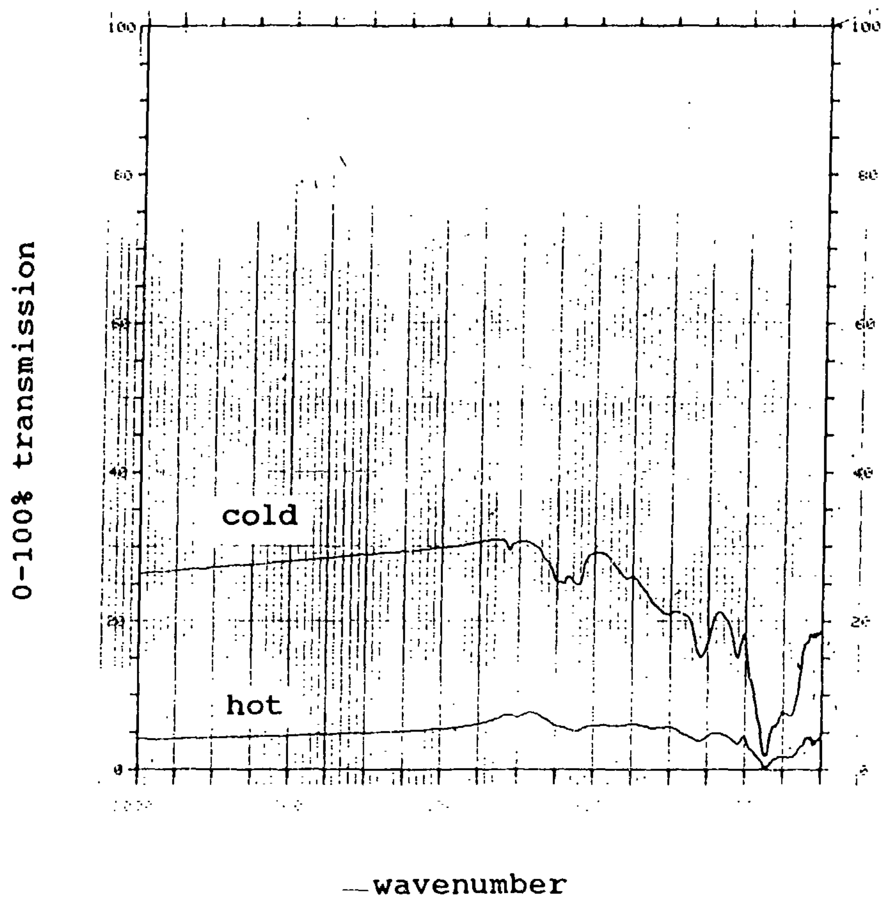

FIGURE 3

Hot and Cold Reflection of Sample Vanadium Dioxide Film

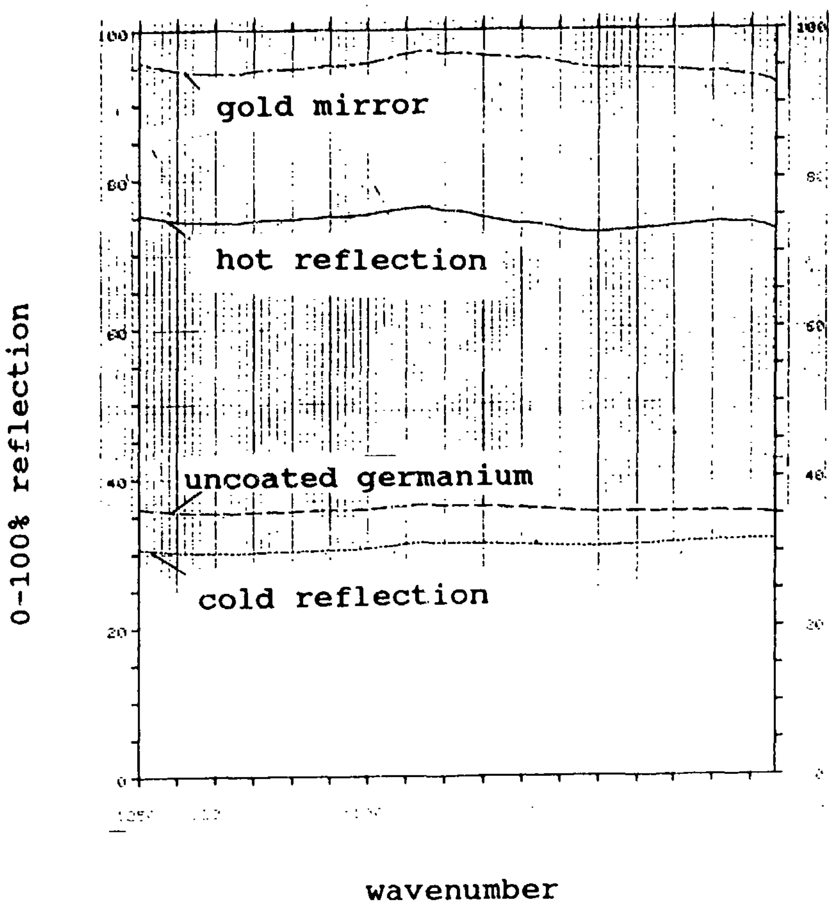

FIGURE 4

Theoretical Transmission of Single Layer Overcoating

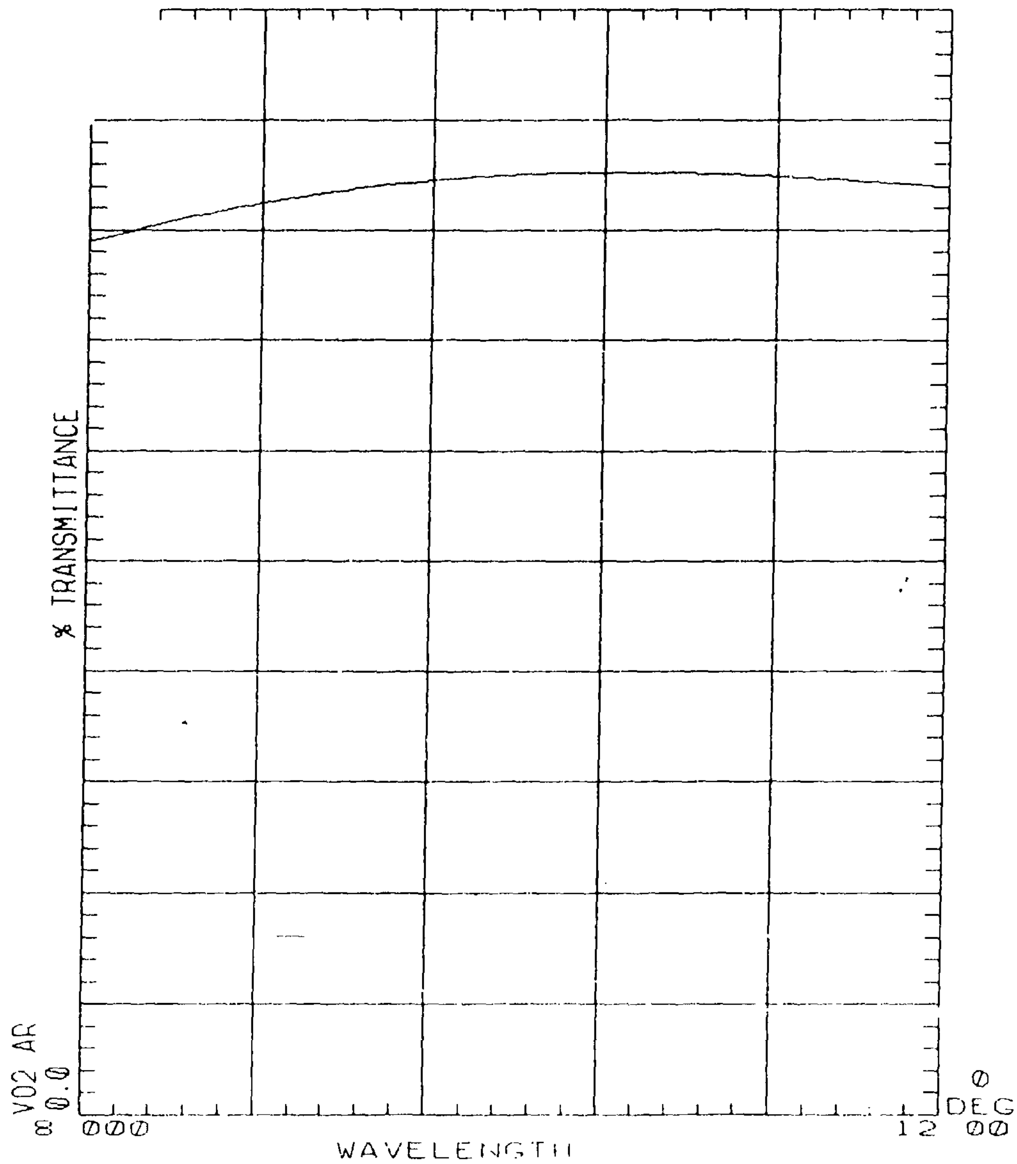

FIGURE 5

Theoretical Transmission of Single Layer
Equivalent Overcoating

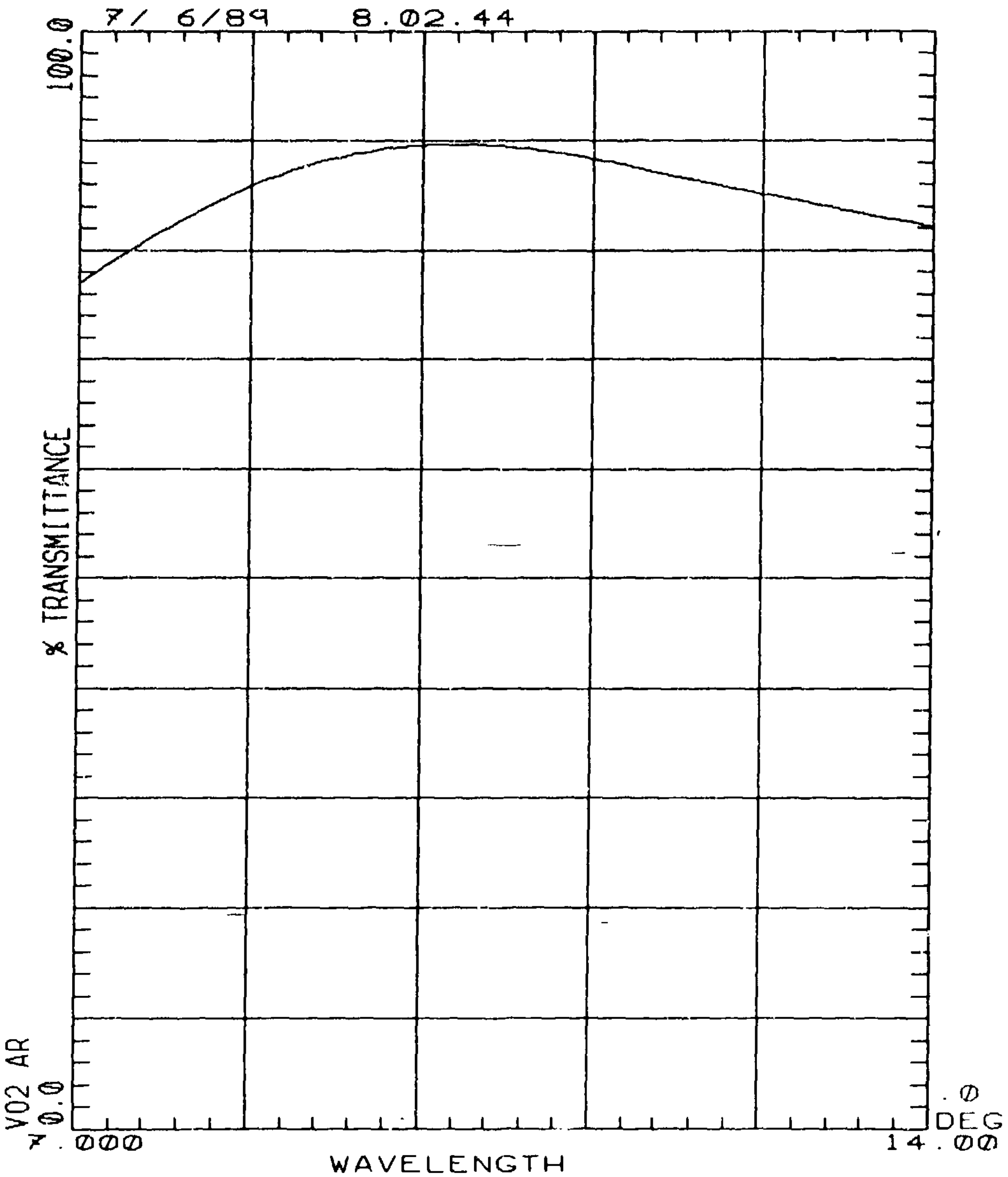

FIGURE 6

Theoretical Reflection of Single Layer
Equivalent Overcoating

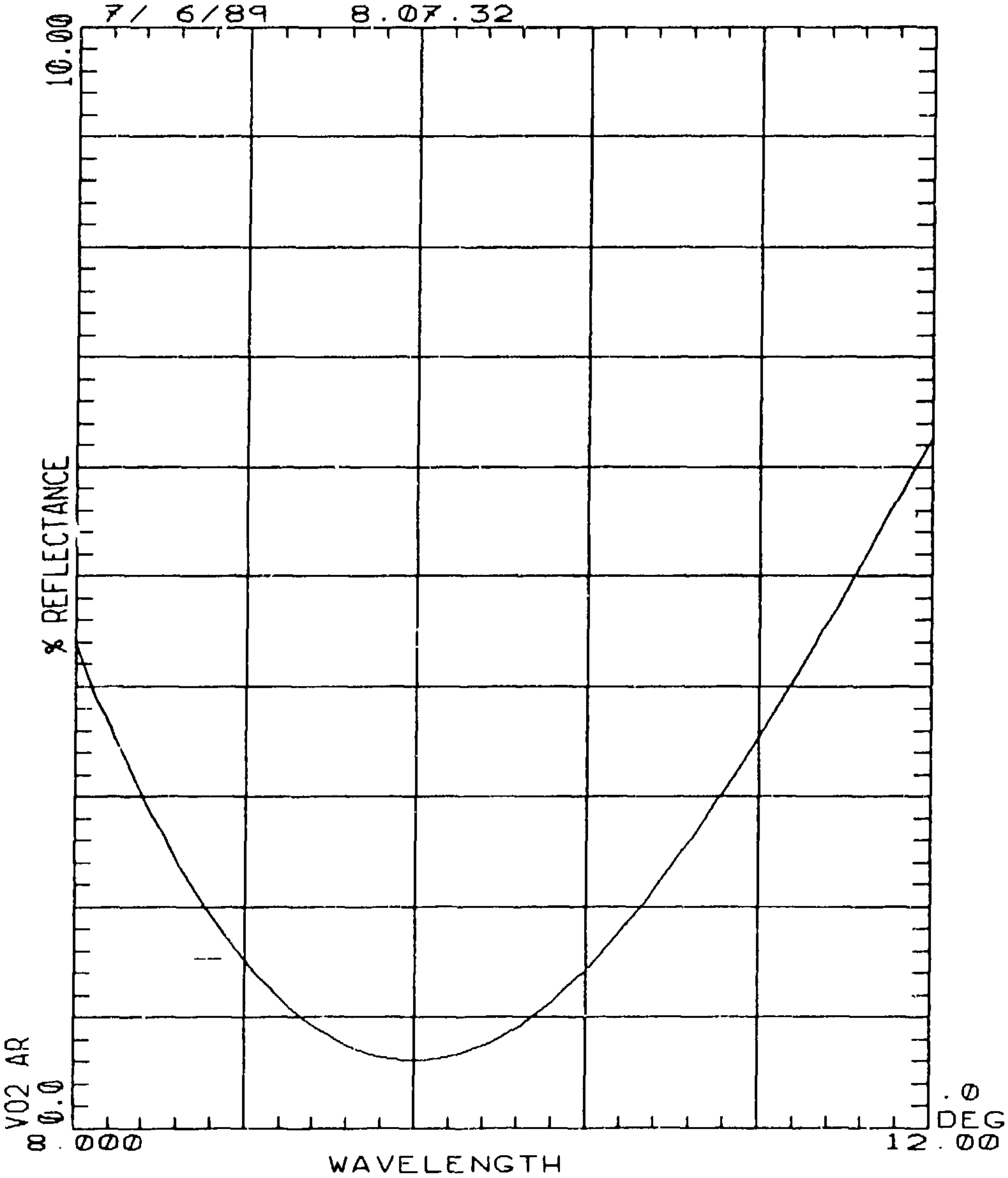

FIGURE 7

Theoretical Vector Amplitude of Single Layer Equivalent Overcoating

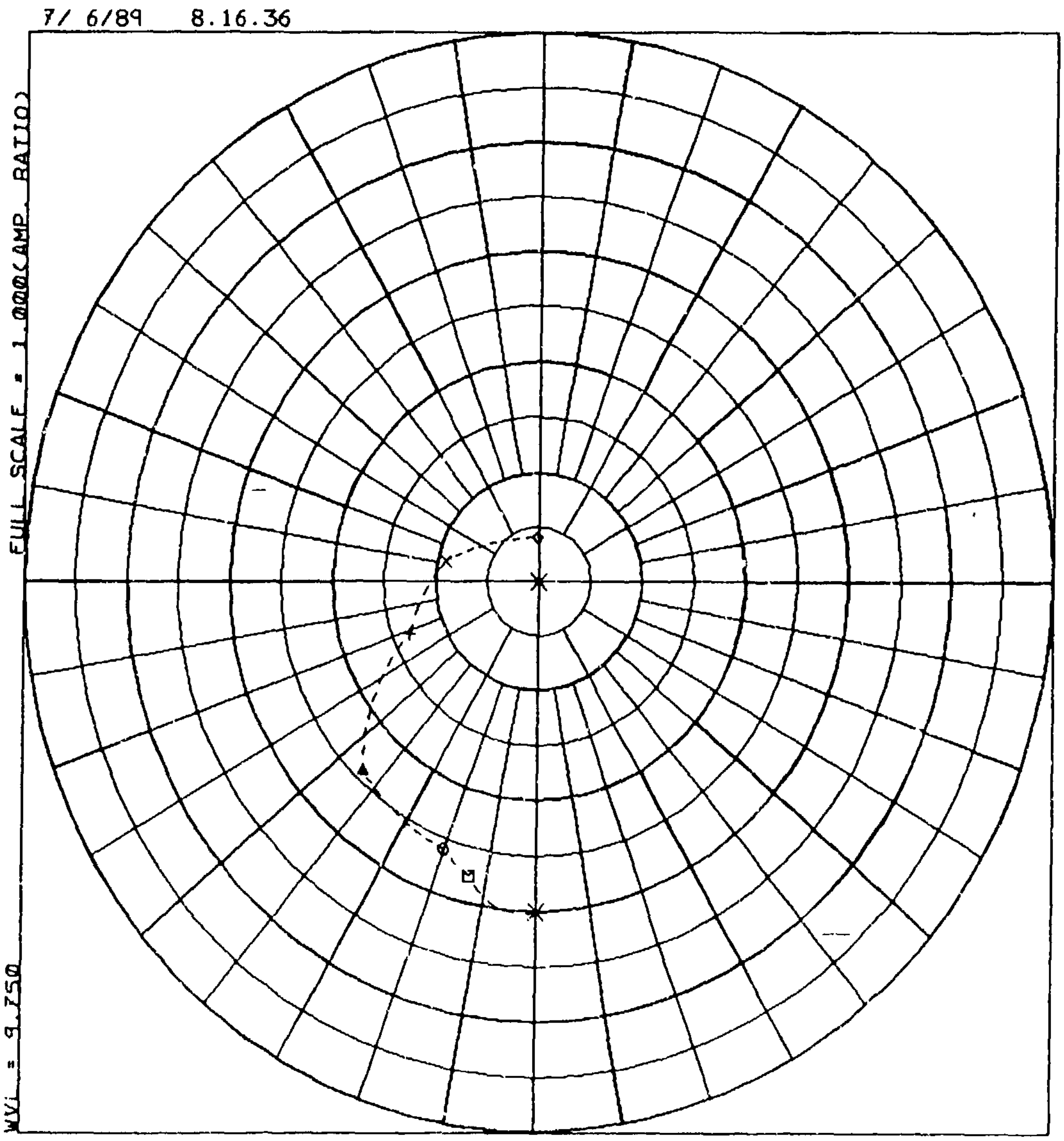

FIGURE 8

Theoretical Transmission of Two Layer Overcoating

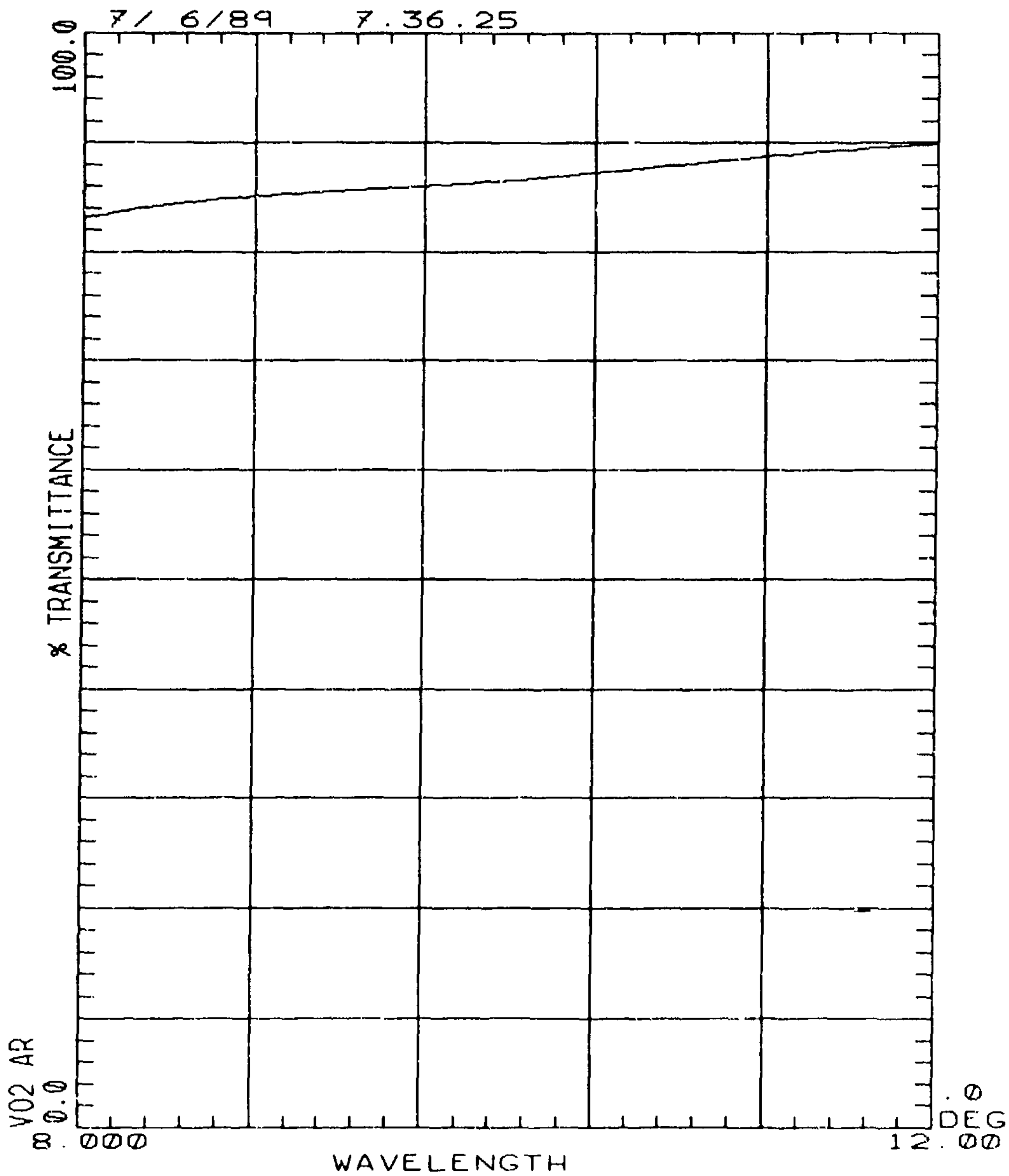

FIGURE 9

Theoretical Reflection of Two Layer Overcoating

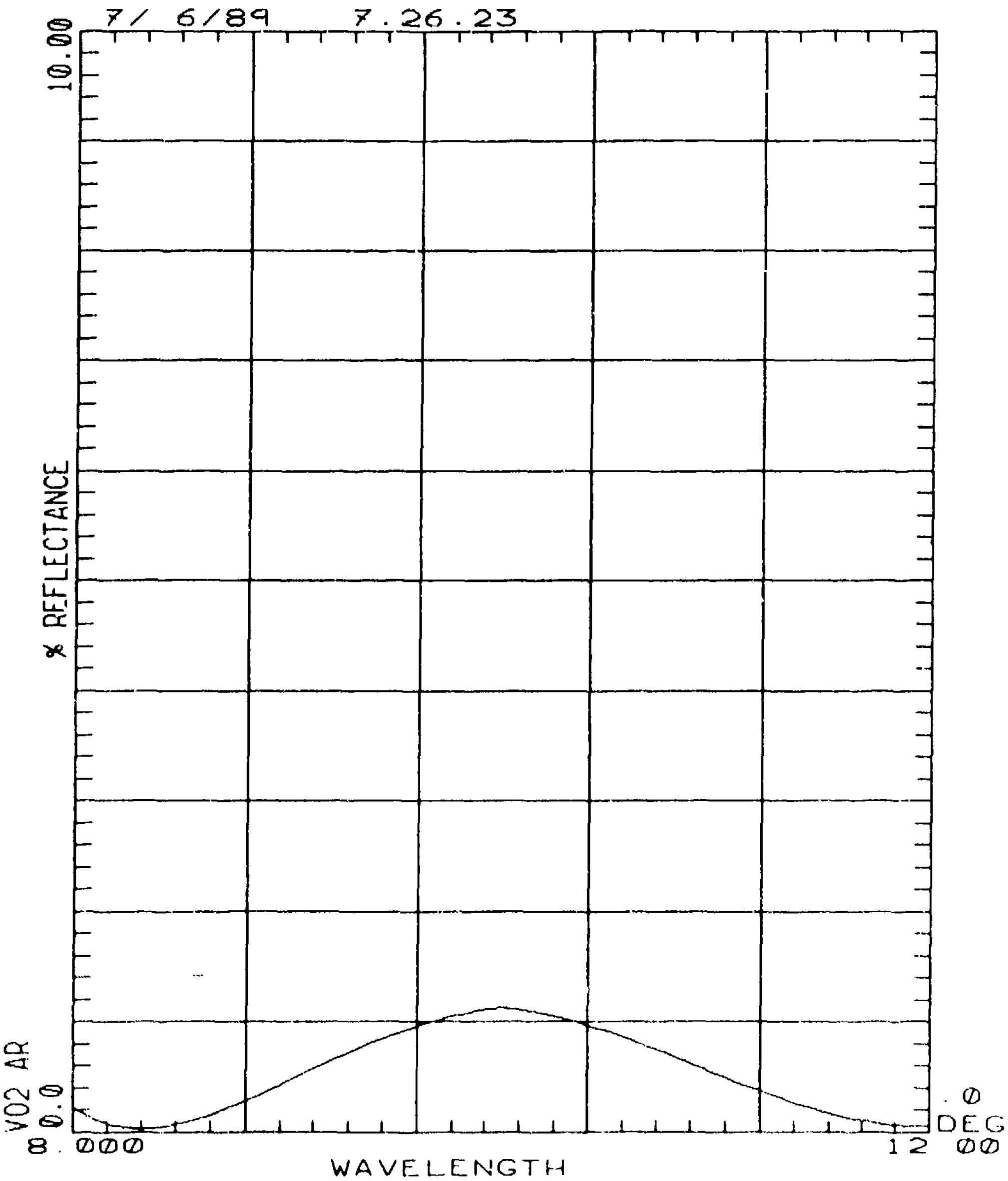

FIGURE 10

Theoretical Transmission of Three Layer Overcoating

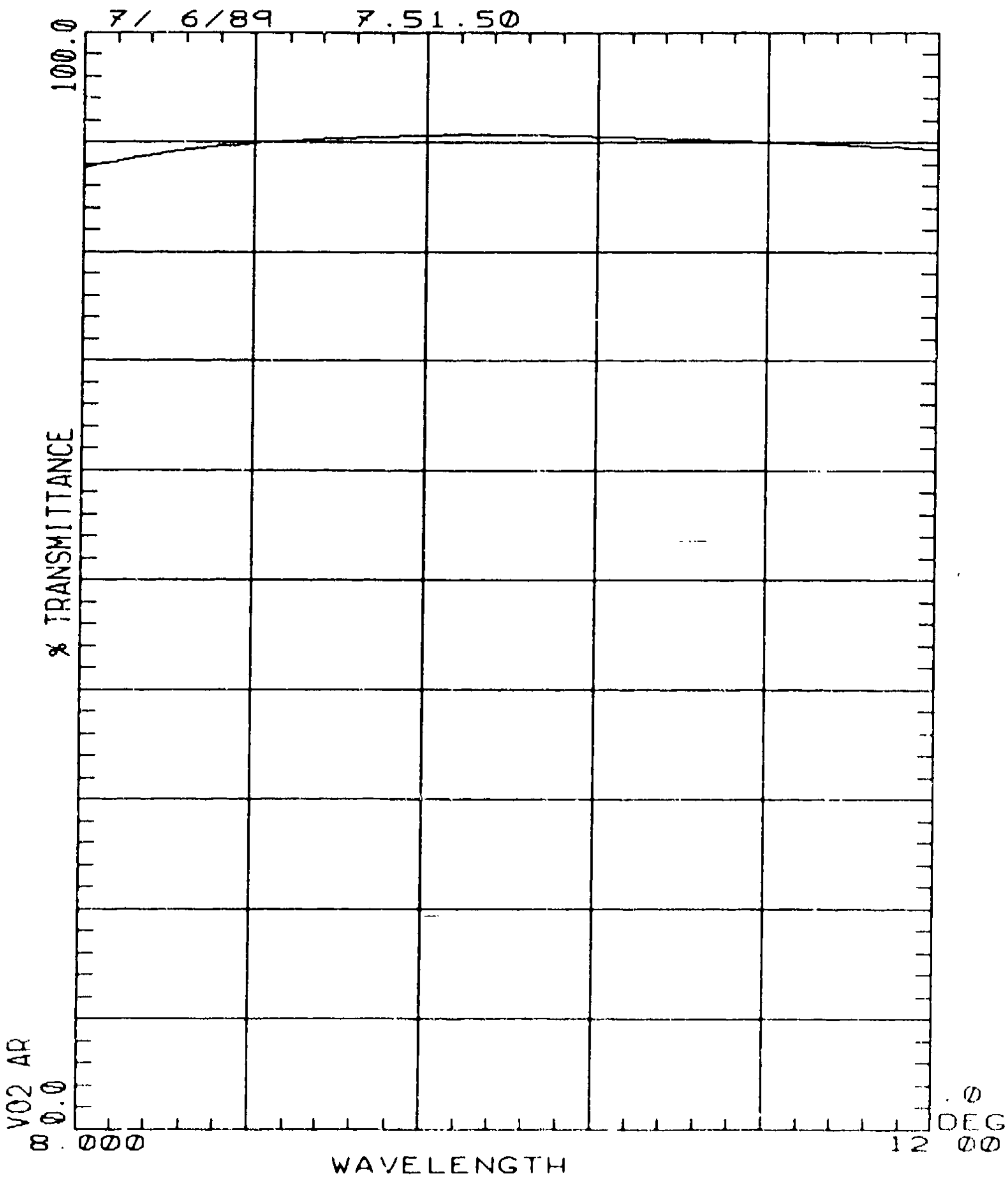

FIGURE 11

Theoretical Reflection of Three Layer Overcoating

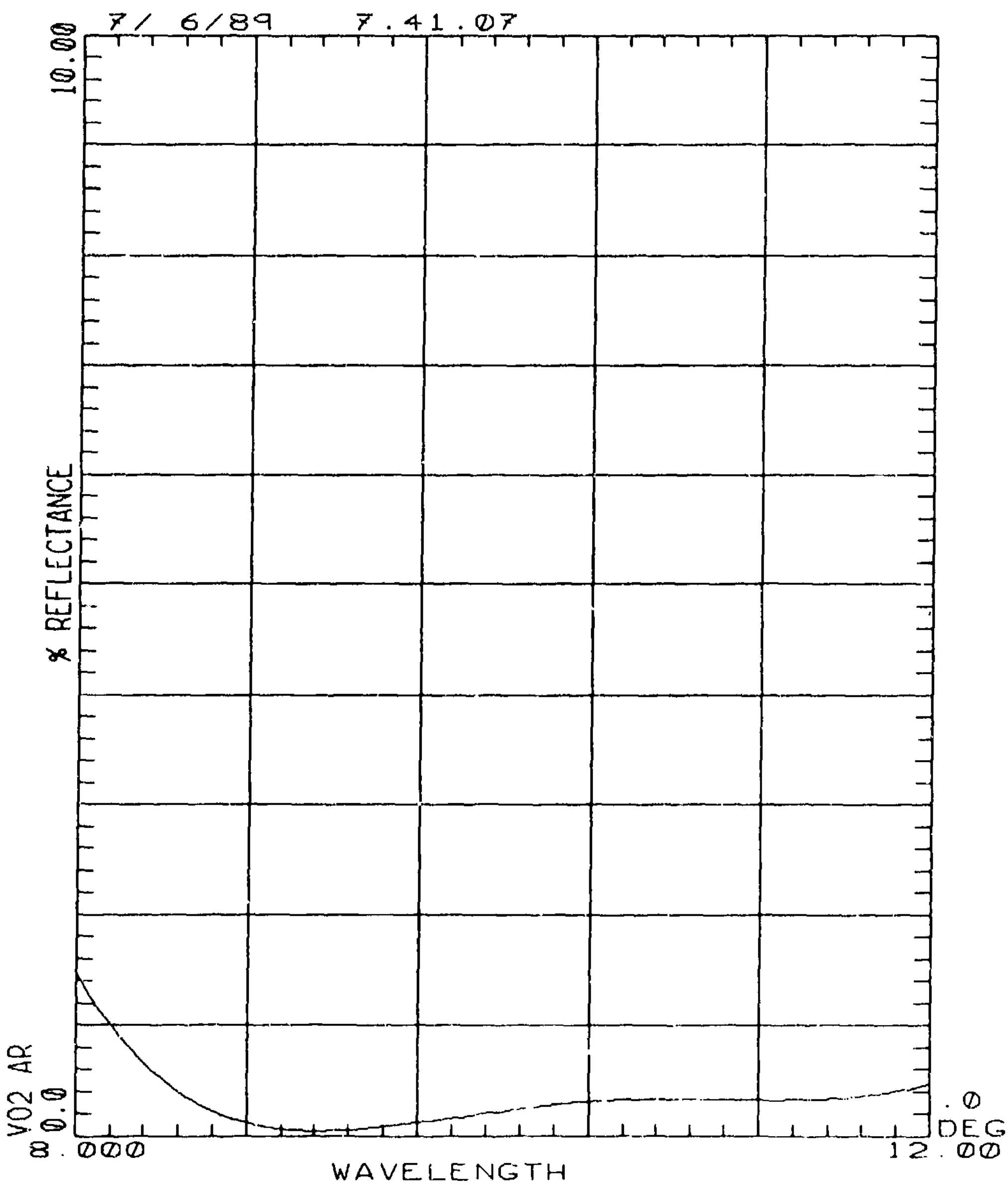

FIGURE 12

Hot and Cold Transmission of Device with Two layer Overcoating

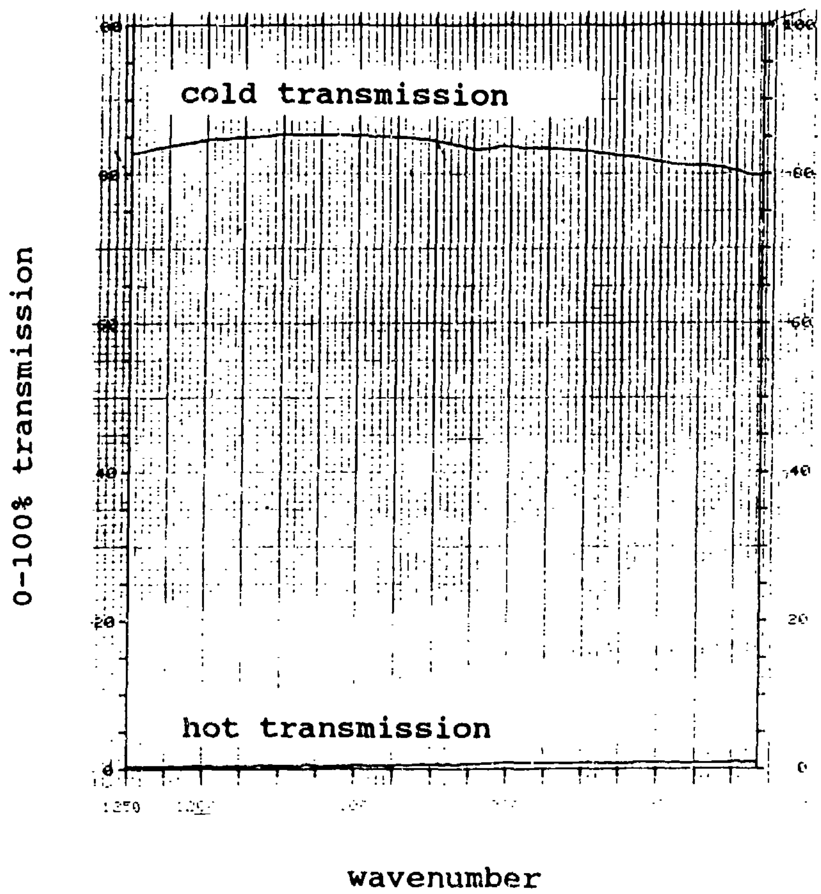

FIGURE 13

Room Temperature Reflection of Device with
Two Layer Overcoating

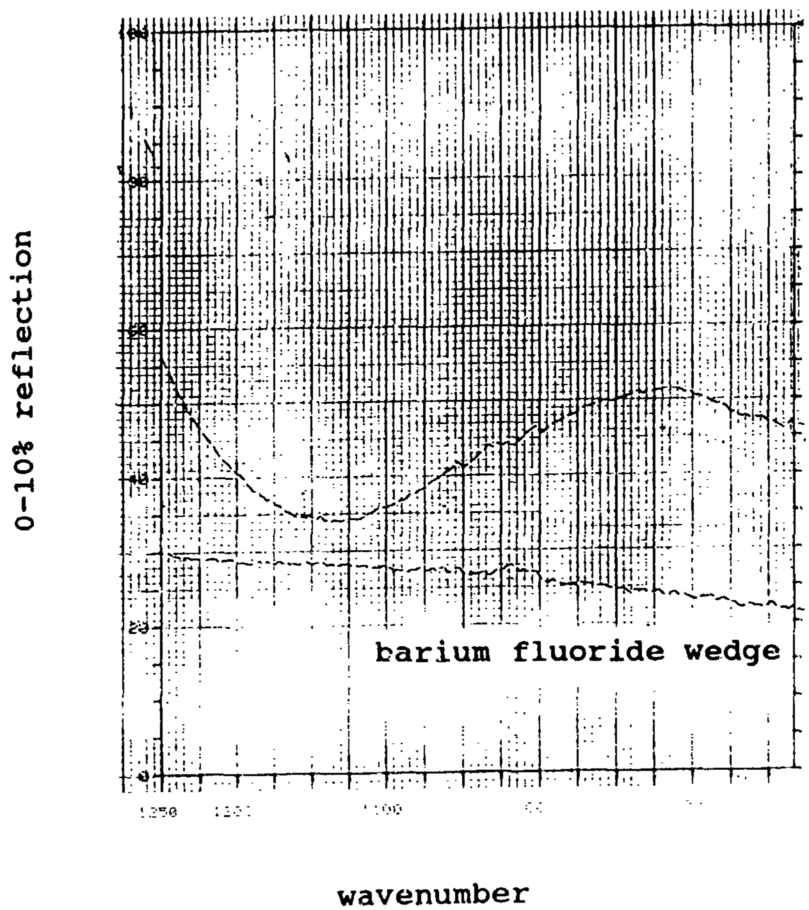

FIGURE 14

Hot and Cold Transmission of Device with
Three Layer Overcoating

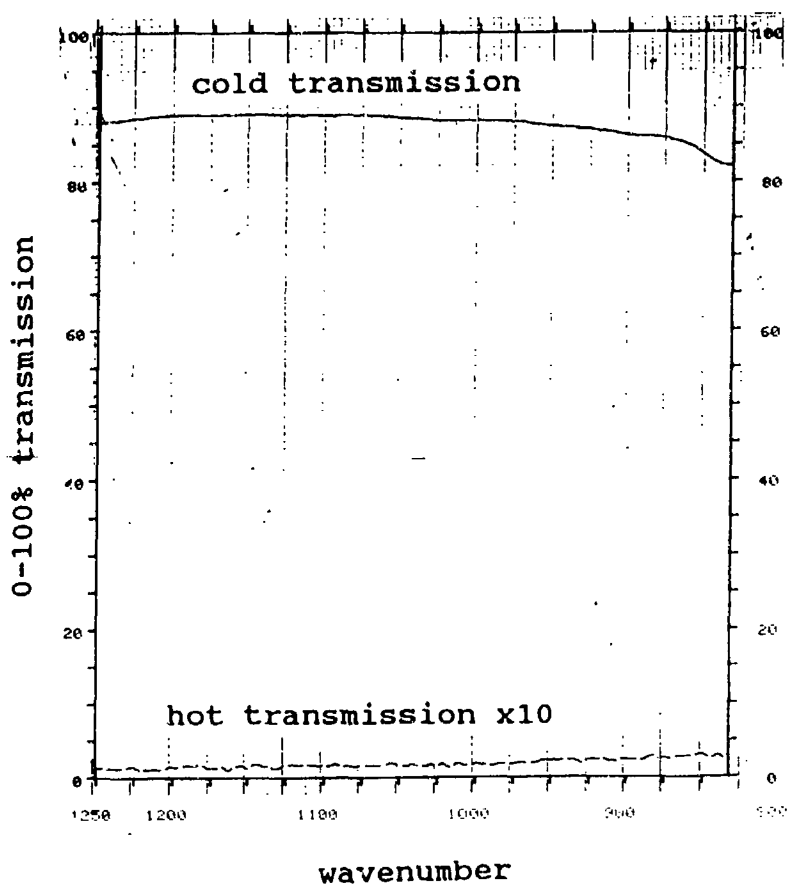

FIGURE 15

Room Temperature Reflection of Device with Three Layer Overcoating

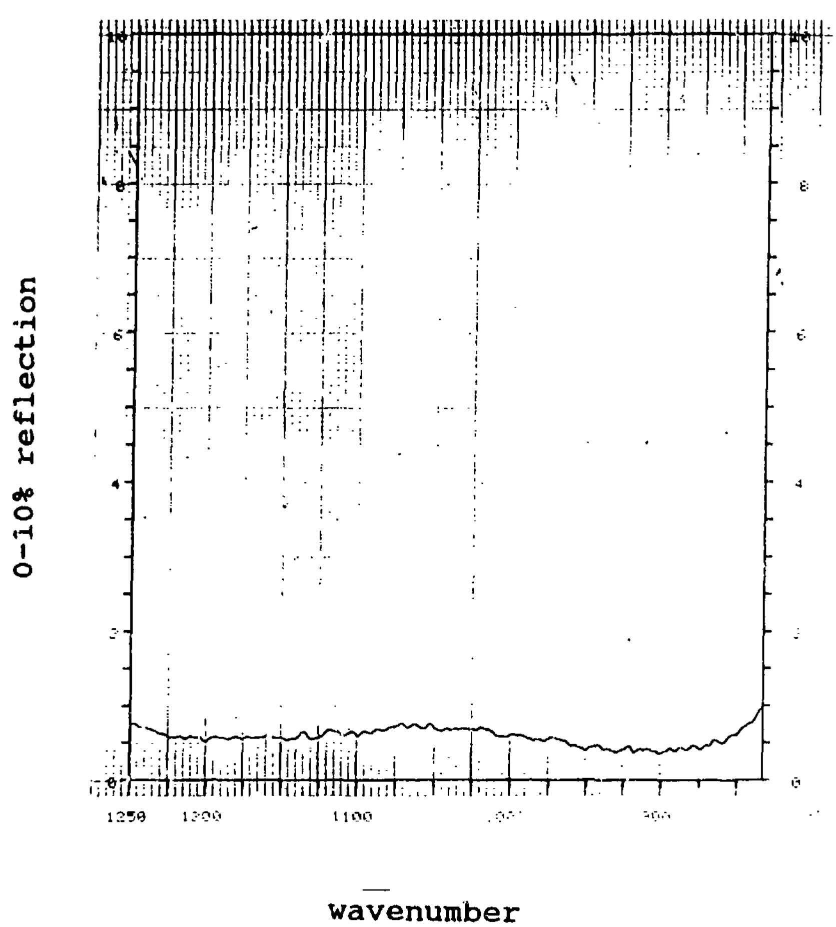

FIGURE 16

Optical Transition of Sample Device